J Sol-Gel Sci Technol (2008) 45:291–297
DOI 10.1007/s10971-007-1672-1

ORIGINAL PAPER

Fast CO_2 sequestration by aerogel composites

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Received: 11 September 2007 / Accepted: 10 December 2007 / Published online: 25 December 2007

Abstract The increasingly evident impact of anthropogenic CO_2 emissions on climate change and associated environmental effects is stimulating the search for viable methods to remove this gas. One of the most promising strategies is the long-term storage of CO_2 in inert, insoluble and thermodynamically-stable materials. This strategy mimics the natural reactions that transform silicates into carbonates regulating the cycle of CO_2 on the surface of the Earth, operating on a geological time-scale. Consequently, the aim is to accelerate these reactions to be applicable on the timescale of human lives. We present the various technologies developed or proposed to date, based on this particular approach. The principal limiting factor is that high pressures and temperatures are required to produce appropriate materials capable of CO_2 sequestration and storage. Nevertheless, the synthetic materials known as aerogels can be modified in shape, size and chemical functionality so as to catalyse the process of CO_2 elimination through silicates (of Ca or Mg), considerably reducing the reaction time and working at atmospheric pressure and temperature.

Keywords Aerogel · Wollastonite · Composite · CO_2 sequestration · Carbonation reaction

1 Introduction

Among the gases contributing to the "green house effect", the influence of CO_2 has been estimated at 40–50% of the total. Currently, the policy proposed for dealing with this problem is the reduction of gas emissions from power generation processes, transport and especially-contaminating industries (such as cement factories). Any viable strategy with this objective requires technologies that incorporate CO_2 elimination processes, i.e., separation, capture (sequestration), disposal or storage and, finally, elimination. Everything must be carried out at costs that are feasible for the gas emitting countries, organisations and industries to bear.

Among the more viable techniques advocated for CO_2 sequestration are chemical absorption, physical and chemical adsorption, low temperature distillation, gas separation membranes, mineralization and vegetation. However, the main drawback of all these processes is that, in one way or another, they consume more energy, which gives rise to additional CO_2 emission. The same can be said about commercial solutions for post-combustion capture, mainly based on amines, which subsequently must be regenerated in order to be re-utilised. These regeneration processes require the temperature of the material to be raised, which

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involves a waste of energy and, consequently, a loss of system efficiency.

Regarding the storage and elimination step, a feasible option that has been proposed is the irreversible fixation of CO_2 in thermodynamically-stable solid materials such as insoluble inorganic carbonates. The fixation is accomplished by a reaction known as mineral carbonation. In a carbonation reaction, the CO_2 reacts with alkaline-earth materials containing metal oxide (mostly silicates), forming the corresponding carbonate and silica as a by-product. From a thermodynamic point of view, the reactions are exothermic because the carbonates have a lower energetic state than the CO_2. Nevertheless, the kinetics of this transformation is very slow, requiring additional intensive energy (activation energy) to increase the mineral reactivity to give economically-feasible reaction times. This reaction accelerates under conditions of high pressure and temperature that involve associated energy costs. Thus, for a technology to be efficient and economic, the reaction rate must be increased without this drawback.

It is known that some natural silicates form carbonate when in contact with CO_2. In particular, the wollastonite ($CaSiO_3$) reacts to produce calcite and silica. This is a natural reaction that has operated over millions of years to reduce the CO_2 in the Earth's atmosphere. Wu et al. (2001) [1] and Tai et al. (2006) [2] have published results on the rate of conversion of wollastonite ($CaSiO_3$) in calcite ($CaCO_3$) for different experimental protocols. These values must be interpreted to determine the efficiency of CO_2 fixation by the minerals. Thus, starting from a powdered wollastonite sample in a reactor at atmospheric and room temperature, Wu et al. obtained 14% of wollastonite converted into calcite after 22 days. Later, a comparative study has been carried out [3] analysing different types of samples and experimental conditions, and has given more encouraging results. Among the options, the results worth noting are those obtained from powdered magnesium silicate under high pressure and temperature conditions, resulting in 80% conversion after 1 h. The critical experimental variables turn out to be sample pulverisation, the chemical species present in the aqueous solution, and high pressure and temperature conditions.

1.1 Aerogels as supports for CO_2 sequestration

The intrinsic properties of the sono-aerogels (very high specific surface area and pore sizes in tenths of one nm) [4, 5] make this materials attractive for use in the adsorption, capture and sequestration of polluting gases. The addition of an active divalent cation silicate promotes CO_2 speciation and its subsequent capture via carbonation reactions in a solid stable phase. The silica aerogel–wollastonite composites permit large amounts of CaO to be hosted [6]. Fine synthetic wollastonite powders have been incorporated into silica aerogels by a sol-gel process and silica aerogel–wollastonite composites with different concentrations of powders have been prepared. This processing method allows the composite to maintain the textural characteristics of aerogel that are found to be very efficient in the process of sequestration to eliminate CO_2. We found that the carbonation reaction is very efficient at atmospheric pressure and room temperature. With no special experimental conditions, the aerogel composites accelerate the carbonation kinetics; a high rate of wollastonite → calcite conversion has been observed in comparison with the rates obtained in natural samples. The conversion reaction, referring to the mineral phase hosted in the aerogel matrix, attains values exceeding 80% in 40 min in composites containing up to 40% by weight of CaO.

Furthermore, the reaction by-products (calcite and silica) have an significant residual value since they can be re-used as a raw material (loading) for several known commercial processes (cement manufacture, coating, mortars,…) depending on their morphology, purity and particle size. For example, the by-products of sequestering the CO_2 produced by a cement plant could be used as major raw materials to fabricate cement. In this way, we could close the emission–sequestration–reutilization loop.

Once the goal of synthesising a high efficiency composite has been accomplished, an essential prerequisite is the reduction of cost before scaling up the process for industrial purposes. Here we present results for aerogel-based composites in which the cost of the active phase (natural or synthetic wollastonite) is lower than that of a previous product [6], although not yet low enough for industrial implementation. As in our previously reported results, the reactions take place at room temperature and atmospheric pressure, which considerably reduces the energy cost.

2 Experimental

Two types of composite were prepared, the difference between them being in the nature of the active phase. Whereas in the first type it is a natural wollastonite mineral from the area of Aroche (Huelva, Spain) [7], in the second composite, the mineral is synthesized by reacting sodium metasilicate and calcium chloride.

2.1 Aerogel–natural wollastonite composite (ANWC)

Raw natural wollastonite (NWP) was milled in an agate mortar and the resulting powder was sieved to <354 μm

(−45 mesh). The powder surface was chemically modified with 3-aminopropyltrimethoxysilane (APMES) in order to facilitate and stabilize a colloidal dispersion into the precursor sol of the host gel matrix. A mixture of APMES/wollastonite powder was diluted in ethanol under vigorous magnetic stirring for 10 min, followed by homogenisation with the help of a high speed rotary blender (Ultraturrax TP 18/10) operating at 20,000 rpm. The slurry was separated by centrifugation and dried in an oven at 80 °C for 24 h. The powder obtained was added, -under ultrasound-assisted (670 J/cm^3) agitation- to a sol previously prepared by hydrolysis and polycondensation of tetraethoxysilane ($TEOS:H_2O:HNO_3 = 1:4:0.026$), also ultrasonically assisted with 670 J/cm^3 of ultrasound energy. The mixture gels in few minutes (∼5 min).

The gel obtained was dried by evacuation in an autoclave to remove the solvent (mostly ethanol) under supercritical pressure and temperature conditions; this resulted in an aerogel/wollastonite composite, which will be referred to in this paper as ANWC. Finally, this composite was heat-treated at 900 °C for 1 h, to give what will be referred to as ANWC900.

2.2 Aerogel–synthetic wollastonite composite (ASWC)

The other batch of wollastonite powder was prepared from a SiO_2–CaO gel, with a silica-to-calcium oxide ratio equal to 1. The gel was obtained from Na_2SiO_3 and $CaCl_2$ solutions. The concentrations of the two reagents were adjusted to 0.1 mol/L and 1:1 volume ratio. A gel containing SiO_2, CaO and nH_2O precipitates immediately according to the reaction:

$$\mathrm{Na_2SiO_3 + CaCl_2 \rightarrow [SiO_2, CaO, nH_2O]_{gel} + Nacl} \tag{1}$$

In this reaction, the pH values are controlled to: pH $CaCl_2$ (0.1 M) = 9.35, pH Na_2SiO_3 (0.1 M) = 10.72 and pH ($CaCl_2$ (0.1 M) + Na_2SiO_3) = 9.51.

Afterwards, the gels were centrifuged (10 min at 1000*g*) and then dried in an oven at 80 °C. The synthetic powder (SWP) was ground and then heat-treated at 900 °C for 1 h. This powder will be referred to as SWP900.

Like the natural wollastonite, this powder was treated with APMES in the way described above. An aerogel composite was prepared in the same way as its natural counterpart ANWC. This composite will be referred to as ASWC. This composite was also heat-treated at 900 °C, and in the rest of the paper will be referred to as ASWC900. Figure 1 shows a scheme of the process followed to obtain the composites.

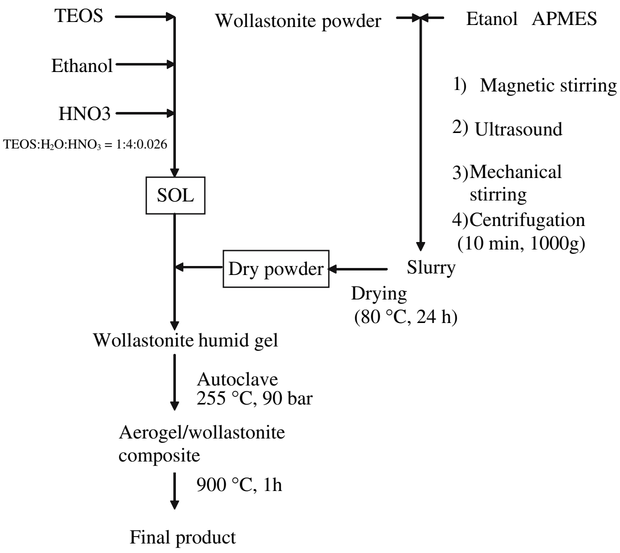

Fig. 1 Flow-chart showing the synthesis routes for the composite materials studied

2.3 CO_2 sequestration set-up

The experiments for monitoring the fixation of CO_2 were carried out in a reactor under agitation. This device consists of a plastic container isolated from the external atmosphere by means of a hermetic stopper, which is pierced and through which a pH electrode is inserted to monitor the variation of this parameter. The container is connected to a CO_2 tank through two valves, for the inlet and outlet of CO_2.

The sample (0.5 g of ANWC900 or ASWC900) was ground, dispersed in distilled water (20 mL). The mixture was submitted to successive flows of CO_2 for 30 min under atmospheric pressure at room temperature. After this time the reactor was left to rest overnight before checking the degree of carbonation of their respective wollastonite contents. The pH was monitored during the experiment. Before injecting CO_2, several drops of $NaHCO_3$ 0.5 M had been added to the distilled water in order to avoid the pH falling to more acidic values once the gas flow started. The pH remained above 7 until the experiment was completed.

Prior to examining their capacity for CO_2 sequestration, the samples were characterised. The compositional and textural features of the samples were determined by X-ray fluorescence (Bruker S4 Pioneer model) and isothermal nitrogen adsorption in an automatic device (Sorptomatic 1990, CE instruments); the Brunauer–Emmet–Teller (BET) method was applied to calculate their specific surface areas. Mercury intrusion porosimetry was carried out in an automatic device (Carlo Erba, Pascal 440) on the de-gassed wollastonite (natural and synthetic) powder: the container is filled with Hg and the sample is pressurized to atmospheric pressure. We take the value measured at this point as the apparent density. For the run, Hg pressure was raised from 0.1 to 300 MPa and it was then depressurized. X-ray diffraction (XRD) experiments were performed on a Bruker diffractometer (D8 Advance) with graphite monochromator and Cu k_α radiation. The intensities were measured in a 2θ range (5°–50°) with a step of 0.2° and a counting time of 5 s per step. The EVA and FULLPROF program were employed for the analysis of the crystallization products (wollastonite powders and carbonates).

In addition the quantity of resulting carbonate was determined by thermogravimetric analysis (TGA) in air (Setaram Setsys 16/18), heating from 20 °C to 900 °C at 10 °C/min.

3 Results and discussion

The chemical composition and textural characteristics of the composites are presented in Table 1.

The pore volume derivatives resulting from the Hg intrusion experiments are represented in Fig. 2. The pore size distribution of the NWP powder is bimodal. A sharp peak is seen at ~5 nm that accounts for the irregular surface resulting from the acicular texture. The second part of the curve is formed by a maximum centred at ~60 nm followed by a long tail; this corresponds to a distribution of grains from ~400 nm size to hundreds of micrometers.

The pore size distribution of the SWP is irregular, presenting a wide distribution. As in the case of the NWP sample, the pore size distribution of the SWP presents a maximum at low r values (r ~ 10 nm), which can also be attributed to the acicular texture, (representing a pore volume at this level two orders of magnitude less than its natural counterpart), followed by a wide range from 10^2 to 10^4 nm. This indicates a wide distribution of particles (they were simply milled in an agate mortar) formed by grains from hundreds of nm up to tenths of microns. As a result of this large grain size the surface/volume ratio of these powders is low and, correspondingly, the pore derivative value of the first maximum is low.

Table 1 Sample characteristics

Sample	Chemical composition		Textural characteristics	
	CaO (%)	SiO_2 (%)	Specific surface area (m^2/g)	Porous volume (cm^3/g)
SWP900	30	68	0.97	0.002
ASWC	18.6	80.3	122	0.21
ASWC900	18.6	80.3	28.7	0.04
ANWC	28.5	70	335.2	0.52
ANWC900	28.5	70	67.7	0.14

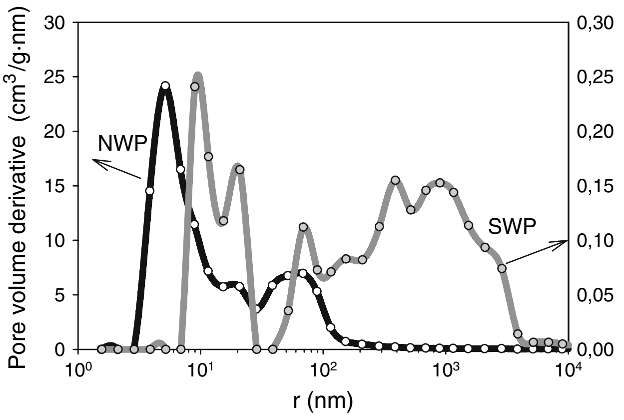

Fig. 2 Pore volume derivative of natural (NWP, black line) and synthetic (SWP, grey line) powders before being submitted to CO_2 flow. The lines are eye-guides. The black line is represented with reference to the left axis, the grey line with reference to the right axis

The X-ray diffraction patterns of the NWP and ANWC samples are shown as Figs. 3 and 4, respectively. The phase present in the NWP sample can be identified as a 1T wollastonite polytype, although the maximum intensities do not completely match the standard of this polytype. This deviation is caused by the existence of specific directions of preferential growth (Fig. 5), which develop an acicular morphology. This phenomenon results in a diffraction profile that displays peaks of different intensity in comparison with those corresponding to the 1T polytype, in particular reflection planes. The preparation of the composite induces additional changes in the intensity of the reflection of those planes and the appearance of new reflections that are consistent with those of a hydrated calcium silicate (Fig. 4). However, the silica matrix hosting the needles of natural wollastonite can be observed (Fig. 6).

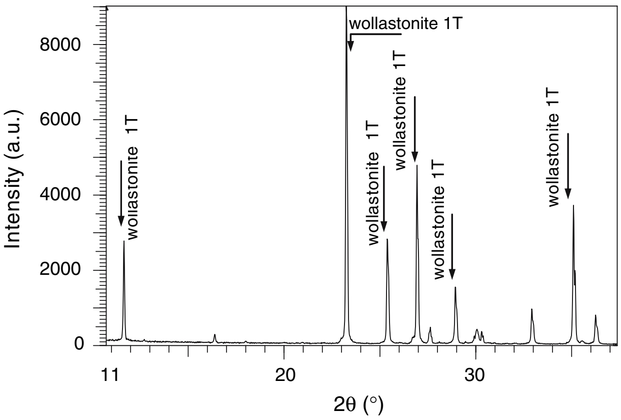

Fig. 3 Standard X-ray diffraction pattern of the raw natural wollastonite powder

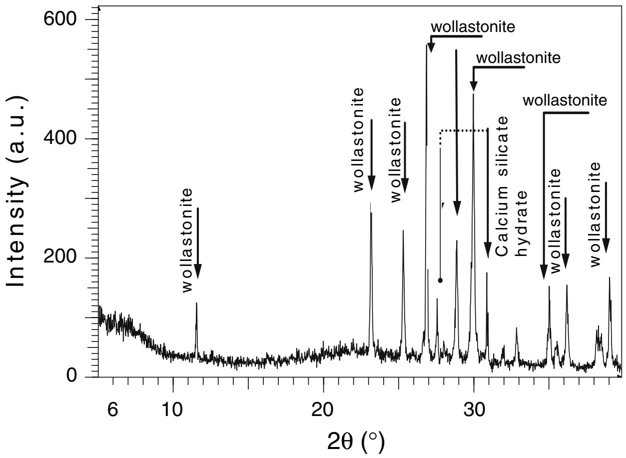

Fig. 4 Standard X-ray diffraction pattern of the aerogel/natural wollastonite powder composite

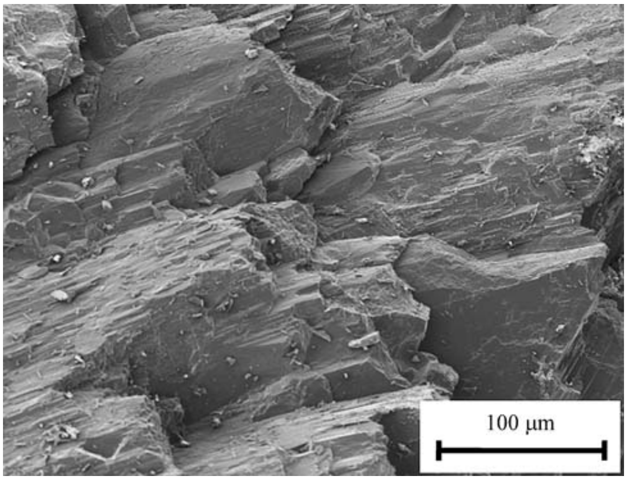

Fig. 5 Micrography of the raw natural wollastonite (NWP)

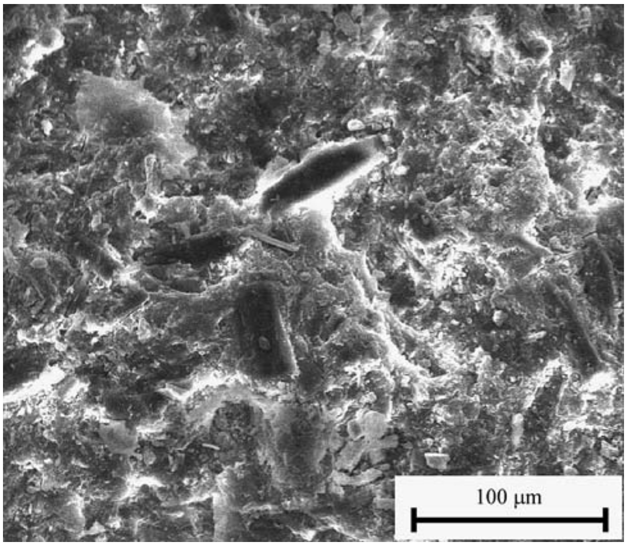

Fig. 6 Micrography of the aerogel/natural wollastonite composite (ANWC)

In the case of the ASWC composite, the active phase is the synthetic powder (SWP) whose chemical composition is indicated in Table 1. Initially the powder is mostly amorphous (Fig. 7). Peaks corresponding to halite, a product of reaction 1, can be seen, as well as a hydrated phase of calcium silicate (tobermorite). The heat-treatment causes wollastonite (1T) to appear (Fig. 8), and this is the mineral species that finally remains in the ASWC900 composite.

In the next stage, the composites were ground and introduced sequentially into the reactor and subjected to CO_2 flow for 30 min. Both gels carbonate quite satisfactorily, as can be inferred from the analysis of the diffraction patterns.

The diffraction profiles of the ANWC900 composite before and after the exposure to 30 min of gas flow are compared in Fig. 9. The carbonated sample has been left to rest overnight before obtaining its diffraction pattern. It can

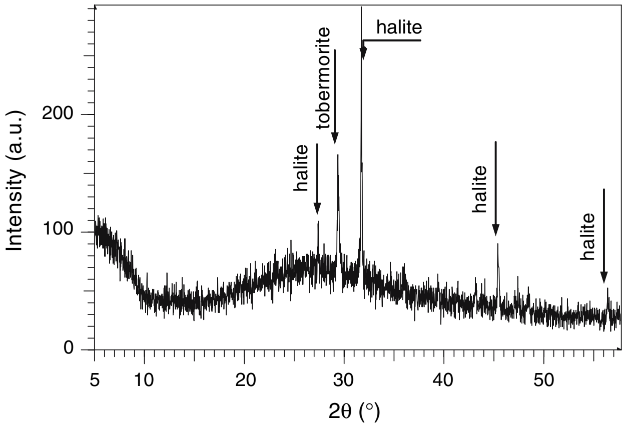

Fig. 7 Standard X-ray diffraction pattern of the synthetic powder, SWP sample

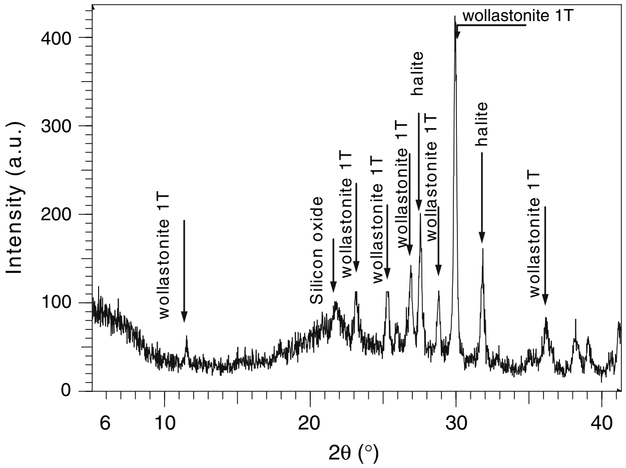

Fig. 8 Standard X-ray diffraction pattern of the SWP900 sample

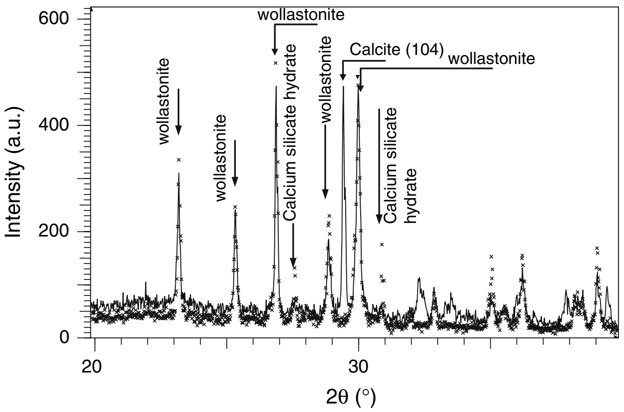

Fig. 9 Diffraction profiles of the ANWC900 composite before and after exposure to 30 min of CO_2 flow

be observed that the intensities of some peaks disappear almost completely (crosses). This difference is attributed to the dissolution of the wollastonite caused by the gas flow; the mineral then reacts to form calcium carbonate (calcite), as can be inferred from the continuous line profile.

In this sample, estimating the carbonation reaction efficiency from the X-ray diffraction profiles analysis involves some difficulties because of the preferential orientation of certain (hkl) planes. For this reason the amount of carbonate that results has been calculated by thermogravimetric analysis. Figure 10 shows the weight loss of the ANWC900 sample. A peak can be observed in the differential curves (TGA and DTG) between 535 °C and 750 °C, which is related to the decomposition of the carbonate according to a previous analysis of a pure carbonate. From the detailed analysis of these data, the efficiency of the conversion reaction that takes place inside the reactor can be evaluated. In this reaction one mol of wollastonite is converted into one mol of calcite according to

$$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2 \qquad (2)$$

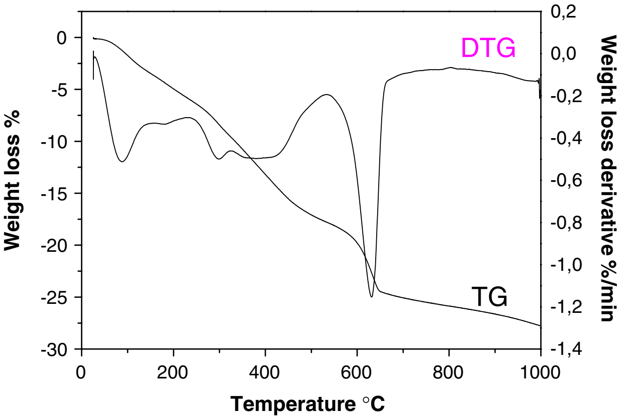

Fig. 10 TGA and DTG curves of the composite ANWC900 after carbonation

Taking into account the composition of the ANWC900 sample, the maximum theoretical weight loss caused by CO_2 release would be about 17%, if all the wollastonite reacted to form calcite. The actual weight loss is approximately 10%. Accordingly the efficiency is estimated to be 60%.

The ASWC900 counterpart is represented in Fig. 11. In this case, the wollastonite is almost entirely dissolved and the calcite peak can be observed standing out from the other peaks. Merely from observation of this figure, the reaction efficiency can be estimated as relatively high. Once both curves are normalized, their analysis reveals that almost 85% of the wollastonite is dissolved.

Finally, before comparing these results with those of the SAWC40 composite described in our previous paper [6], it is important to note that the CaO content of this composite is 40% by weight, whereas the ANWC900 and ASWC900 composites contain 30% and 18%, respectively. These differences are manifested in their textural characteristics. Although their respective specific surface areas are less than in the former case, they are high enough—when compared to natural non-encapsulated (Ca or Mg) silicates—for the reaction to maintain high values of efficiency. These values are comparable with those of our previous work and can therefore be considered excellent.

Furthermore, since the active phases of the composites presented in this paper are inexpensive, the cost is reduced by 80%. However, this is not the only advantage that makes this strategy affordable, since the reaction by-products (amorphous silica particles and fine calcite crystals, as these shown in Fig. 12) also have a significant

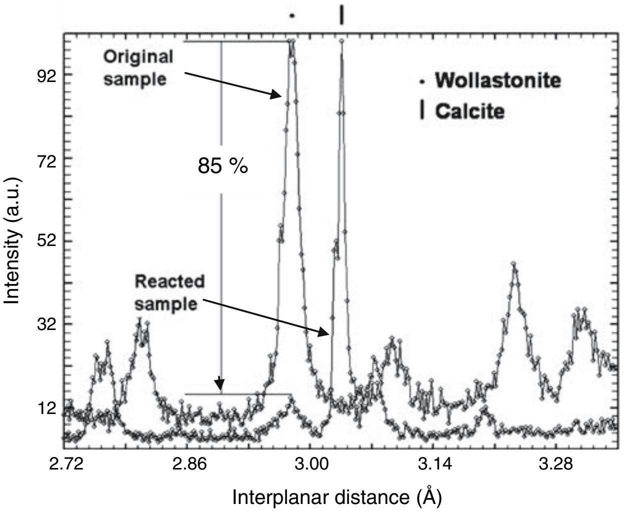

Fig. 11 Diffraction profiles of the ASWC900 composite before and after exposure to 30 min of CO_2 flow

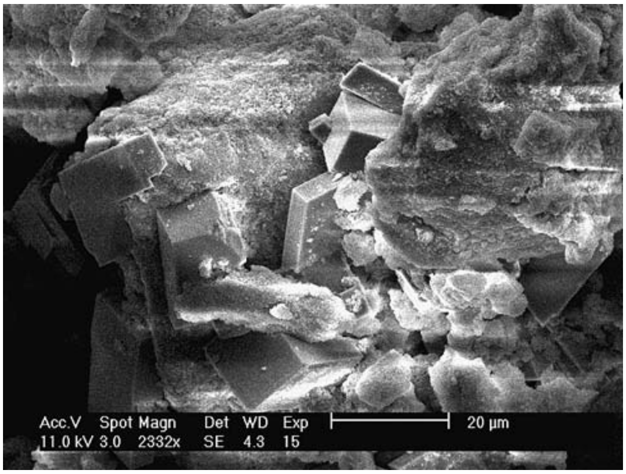

Fig. 12 SEM of the by-products of the ASWC900 composite after exposure to 30 min of CO_2 flow (by courtesy of Víctor Morales-Flórez). There can be observed the individual monocrystals (rhombohedric-like) of carbonates together with unreacted silica gel

residual value. For these reasons, these composites raise realistic expectations as an economically-viable technology for CO_2 capture and elimination.

4 Conclusions

Under the proposal presented, which yields inert and solid by-products, the following advantages are demonstrated:

1. A process for CO_2 sequestration that mimics the natural process occurring on a geological timescale, offers gas capture and fixation at costs considerably lower than those obtained in our previous results. The final product has an intrinsic residual value, being potentially useful in applications like cement industry and construction.
2. The preliminary results show that the composites presented in this paper have textural properties different from those presented in our previous study, the CaO content being different.
3. Both samples containing natural and synthetic wollastonite as the active phase present a satisfactory performance in capturing CO_2 at room temperature and atmospheric pressure.
4. The processing cost of both composites is 80% less than the product we previously reported. This economic improvement is considered sufficiently encouraging in a process of cost reduction for these materials to be financially viable as a technology for CO_2 sequestration.

Acknowledgments The authors are grateful to the Spanish Ministerio de Educación y Ciencia, the Consejería de Innovación Ciencia y Empresa of the Junta de Andalucía (Spain) and Agencia Española de Cooperación Internacional for supporting this work with the Projects MAT2005-01583, TEP790 and AECI A/5575/06, respectively.

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